

THE AQUEOUS ALTERATION OF CR CHONDRITES: EXPERIMENTS AND GEOCHEMICAL MODELING. M. Perronnet¹, G. Berger², M. E. Zolensky¹, M. J. Toplis³, V. M. Kolb⁴, M. Bajagic⁴, ¹NASA JSC (2101 Nasa road one, Mail code KT, Houston, TX 77058-3696, USA, murielle.c.perronnet@nasa.gov, michael.e.zolensky@nasa.gov), ²LMTG ³DTP (14 avenue E. Belin, 31400 Toulouse, France, berger@lmtg.obs-mip.fr, toplis@ntp.obs-mip.fr), ⁴ University of Wisconsin-Parkside (Kenosha, WI 53141, USA, kolb@uwp.edu).

Introduction: CR carbonaceous chondrites are of major interest since they contain some of the most primitive organic matter known (e.g. [1], [2]). However, aqueous alteration has more or less overprinted their original features in a way that needs to be assessed. This study was initiated by comparing the mineralogy and modal abundances of the most altered CR1 chondrite, GRO 95577, to a less altered CR2, Renazzo [3, 4]. Calculated element distributions imply that GRO 95577 may result from aqueous alteration of Renazzo by an isochemical process on their parent asteroid, whose mineralogical composition was estimated ('Unaltered CR' in Table 1).

Table 1. Modal abundances in Renazzo, GRO 95577, CRs and unaltered CR parent-body.

	Renazzo vol% ^[4]	GRO 95577 vol% ^[4]	CRs vol% ^[7,9]	Unaltered CR vol% ^[4]
Kamacite	0.7	0.2		4
Low-Ni kamacite	3.3	2.3		0
Magnetite	0	1.1		0
Pyrrhotite	0	1.1		0
Intermediate S phases	0.9	5.0		0
Total opaque phases	4.9	9.7	4.8-10.2	4
Matrix	47.9	45.6	29.7-63	50
Olivine	19.2	0		19.5
Pyroxene	23.0	0		23
Vermiculite	0	25.2		0
Feldspathic mesostasis	2.8	0		3.5
Chamosite mesostasis	1.4	0		0
Clinocllore mesostasis	0	13.2		0
Total chondrule	46.4	38.4	37-63.1	46
Ca-carbonate	0.8	6.4		0

In the present study, laboratory alteration experiments were performed on mineralogical assemblages whose composition was as close as possible to that of the unaltered CR parent-body. The mineralogy of reaction products was compared to that of Renazzo and GRO 95577 in order to estimate the conditions under which alteration occurred. Experimental results were also compared to predictions of geochemical modeling.

Methods:

Images and chemical analyses. The composition of silicate minerals and opaque phases were determined before and after experiments using a JEOL JSM-5910LV Secondary Electron Microscope (SEM) and Cameca SX-100 electron microprobe in WDS mode. Appropriate silicate and metal standards were used and analyses were performed at 15 keV accelerating voltage, 20 nA beam current and 1 µm spot diameter.

Experiments of aqueous alteration. From oxygen isotopic data and the presence of serpentine/smectite in CRs, the temperature of aqueous alteration on the CR

parent-body has been estimated to be between 0 and 300°C [5-8]. The abundance of FeNi metal and sulfides indicates a low fugacity in O₂ and a high fugacity in S₂. Preliminary experiments were performed at 250°C for a duration of 1 month using pure distilled water in anoxic Paar bombs (log fO₂=-6). The system was closed such that the chemical conditions were buffered by the mineralogical assemblage. In order to identify the elementary reactions, six sub-assemblages were used (Table 2). The objectives were to understand the reactivity of silicates within chondrules (SA1); the influence of FeNi metal within chondrules (by comparing SA1 and SA2); the influence of FeNi metal-sulfides on the reaction within chondrules (by comparing SA2, SA3 and SA4); the reactivity of silicates and metals in the matrix (SA5); the influence of organic matter in the matrix (by comparing SA5 and SA6). Moreover the influence of water/rock ratio (W/R=1 or 40) was tested for whole "synthetic unaltered CR chondrites" (A7-3 and A7-4).

Table 2. Mineralogical assemblages.

	Reagents
SA1	Forsterite + Pyroxene + Feldspar
SA2	Forsterite + Pyroxene + Feldspar + FeNi metal
SA3	Forsterite + Pyroxene + Feldspar + Pyrrhotite
SA4	Forsterite + Pyroxene + Feldspar + FeNi metal + Pyrrhotite
SA5	Fayalite + FeNi metal + Pyrrhotite
SA6	Fayalite + FeNi metal + Pyrrhotite + Organic Matter
A7-3	Forsterite + Pyroxene + Feldspar + FeNi metal + Pyrrhotite + Fayalite
A7-4	Forsterite + Pyroxene + Feldspar + FeNi metal + Pyrrhotite + Fayalite + Organic Matter

We used pure minerals (forsterite Fo, fayalite Fa, clinopyroxene CPX, anorthite An, FeNi metal from Chinga, pyrrhotite Po), whose compositions were checked by EMPA. Maillard products were used as an analogue of CR Organic Matter (O.M.) because they share similar functional groups [10].

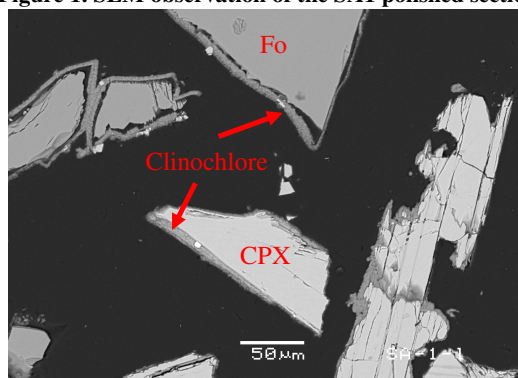
Geochemical modeling. The Geochemist Workbench software was used to model the reactivity of unaltered CR parent-body and sub-assemblages (Table 2) after 1 month at 250°C for the same conditions as the laboratory experiments. Thermodynamic data from thermo.dat database were computed. Using the EQ 3/6 software, the data on kamacite 83 and pentlandite were calculated. O.M. was tentatively described by benzene_{aq}, phenol_{aq}, toluene_{aq} and CH₃COOH_{aq}. The kinetic laws for non-oxidative dissolution of minerals were defined.

Results:

Experiments of aqueous alteration. The silicates within the chondrule assemblage (SA1) are altered to

clinocllore, An being completely eliminated (Figure 1). The alteration of FeNi metal or Po liberates Fe which is incorporated into clinocllore (SA2 and SA3). Po favors the alteration of Fo but this is no longer true when FeNi metal and Po are both present (SA4). On the contrary, for the matrix assemblage, formation of clays is very limited (SA5). This may be due to the absence of An in the matrix assemblage, such that no Al is available. When O.M. is present in the matrix, no clay formation is observed (SA6). On the contrary, when the constituents of matrix and chondrule are in contact, clays are formed and their formation is favored by an increase in the W/R ratio (A7-3 and A7-4).

Figure 1. SEM observation of the SA1 polished section.



The reaction products in chondrule (SA1 to SA4) are TOT O' clays whose composition is characterized by $\text{Si} > \text{Al} > \text{Mg} > \text{Fe}$. These products are quite similar to the alteration products found in GRO 95577 chondrules, which are vermiculite in the core ($\text{Si} > \text{Mg} > \text{Fe} > \text{Al}$) and clinocllore in the mesostasis ($\text{Si} > \text{Mg} > \text{Fe} \approx \text{Al}$). It was not possible to get good chemical analyses of the experimental phyllosilicates formed in the matrix assemblages, and therefore not possible to compare them to the phyllosilicates in the matrix of GRO 95577.

The slight difference in composition between the experimental alteration products of the chondrule assemblage and those in chondrules of GRO 95577 may result from the short duration of the experiments. During the initial stages of the experiment, alteration of An dominates that of Fo or CPX, explaining why experimental clays are richer in Al than natural samples, which experienced longer term alteration. The low level of clay formation in the presence of O.M. indicates that organics may inhibit silicate alteration. However, despite the slower alteration of silicates in the presence of O.M., for the longer durations and smaller grain sizes typical of the alteration of natural matrix, transformations of the silicate phases may take place.

Geochemical modeling. Only the results for the chondrule assemblage are presented since it is the

system for which there is the best match between the natural sample and the reaction products. GWB predicts the consumption of An and Fo, the alteration of CPX and the neoformation of clinocllore in chondrule.

This is in good agreement with the SA1 reaction products and chondrule mineralogy of GRO 95577. Nevertheless the modeling predicts complete elimination of Fo, whereas this mineral remains in the experiments. The poor agreement in terms of reaction kinetics (despite good agreement in terms of mineralogy) may be due to the formation of a protective nanometric layer at the surface of Fo. Moreover GWB uses the Transition State Theory law, which does not take into account the influence of surface properties of minerals (defects, energetic heterogeneities) on kinetic laws [11].

Conclusions:

This work shows that the aqueous alteration of CR parent asteroid may have occurred at 250°C in an anoxic medium without any S_2 flow and in the presence of pure water. It also illustrates the great influence of Al, produced by breakdown of the feldspathic mesostasis, of Po and of O.M. on the crystallization of clinocllore. Al seems to be necessary while Po favors the formation of these clays on Fo unlike O.M. This latter point may be due to the kind of O.M. used. Maillard products seem to have been decomposed into oil which wet the surfaces of silicates and thus inhibited their alteration. New alteration tests with other organics will start in March 2007. Moreover, the geochemical modeling gives good prediction of the evolution of the system from a thermodynamic point of view whereas the kinetic aspect needs to be refined. As future work, other experiments will be conducted at different temperatures, longer term and under CO_2 and H_2S fluxes. Modeling work will be refined to constrain long-term predictions.

References:

- [1] Ash R. D. et al. (1993) *Meteoritics & Planet. Sci.*, 28, 318 [2] Abreu N. M. et Brearley A. J. (2006) *69th Metsoc*, Abstract #5372 [3] Perronnet M. et Zolensky M. E. (2006) *LPS XXXVI*, Abstract #2402 [4] Perronnet M. et al. Submitted to *Meteoritics & Planet. Sci.* [5] Clayton et al. (1977) *Meteoritics*, 12, 199 [6] Zolensky M. E. (1991) *Meteoritics*, 21, 414 [7] Weisberg et al. (1993) *Geochim. Cosmochim. Acta.*, 57, 1567-1586 [8] Kallemeyn et al. (1994) *Geochim. Cosmochim. Acta.*, 58, 2873-2888 [9] Smith C. et al. (2004) *Meteoritics & Planet. Sci.*, 39, 2009-2032 [10] Kolb V. M. et al. (2005) Proceedings of SPIE 5906, 5906OT [11] Perronnet M. et al. (2006) *Geochim. Cosmochim. Acta*, doi: 10.1016/j.gca.2006.12.011

The aqueous alteration of CR chondrites: experiments and geochemical modeling.

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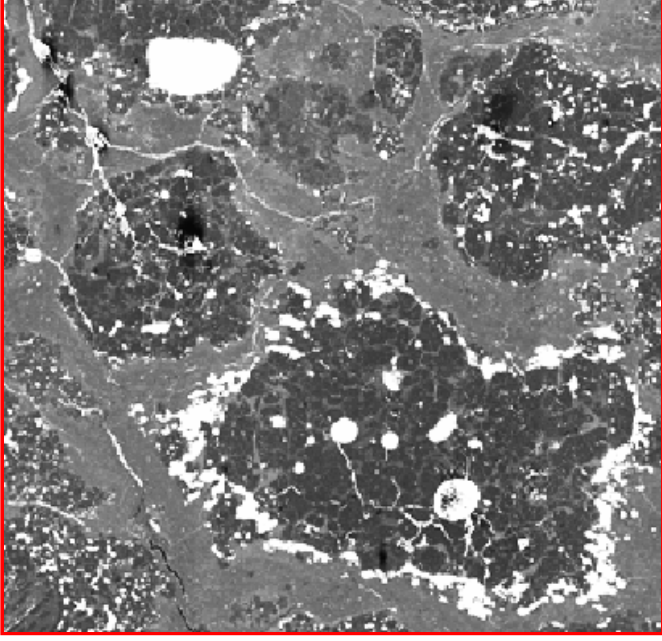
Gilles Berger & Mike Toplis
Observatoire Midi-Pyrénées, Toulouse

Vera Kolb & Milica Bajagic
University of Wisconsin-Parkside, Kenosha

Objectives

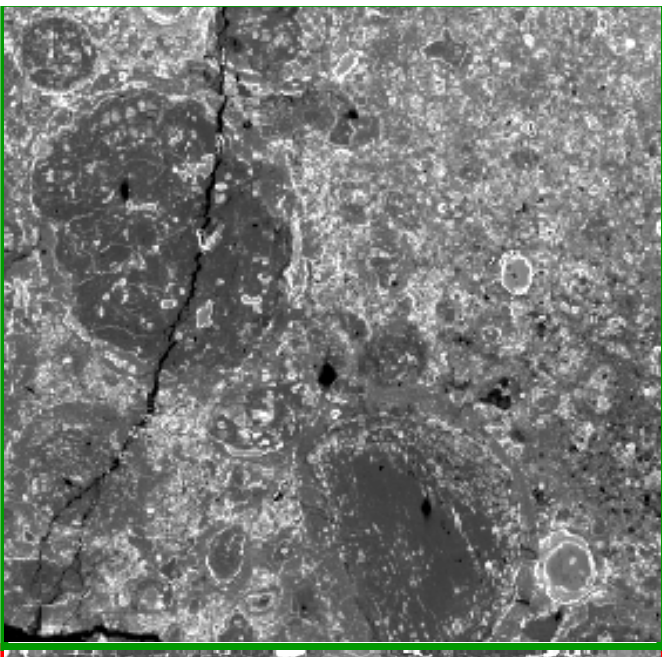
The aqueous alteration of CRs

Renazzo



1 mm

GRO 95577



CR 2

CR 1



- mineralogical transformation ?
- original composition of CRs ?
- influential mineral phases ?
- physico-chemical conditions ?

1. Characterization of CR chondrites

Step 1

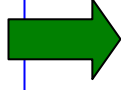
SEM images

EMPA chemical analyses

Modal analysis

using X-Ray elemental mapping
and IDL image treatment software

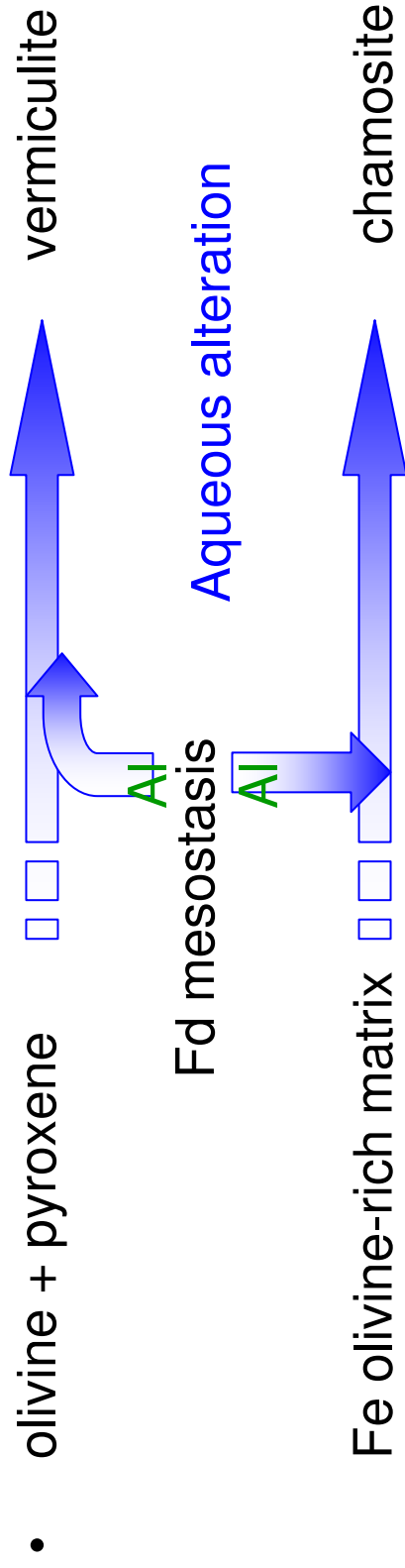
on **Renazzo** (CR2) and **GRO 95577** (CR1)



- Images, composition, abundance of each phase
- Estimation of the **composition** of the **unaltered CR body**

1. Characterization of CR chondrites

1. New data on the mineralogy of Renazzo and GRO 95577.
2. Phenomenological information on the aqueous alteration process
 - unusual petrologic type 1 : limits of chondrule are still visible in GRO 95577
→ chemical alteration without major mechanical process



3. Modal analysis

1. Characterization of CR chondrites

vol% = area% for prismatic crystals

	R	G	CR
Olivine	19.2	0	19.5
Pyroxene	23	0	23
Vermiculite	0	25.2	
Feldspatic meso.	2.8	0	3.5
Chamosite meso.	1.4	13.2	
Chondrules	46.4	38.4	

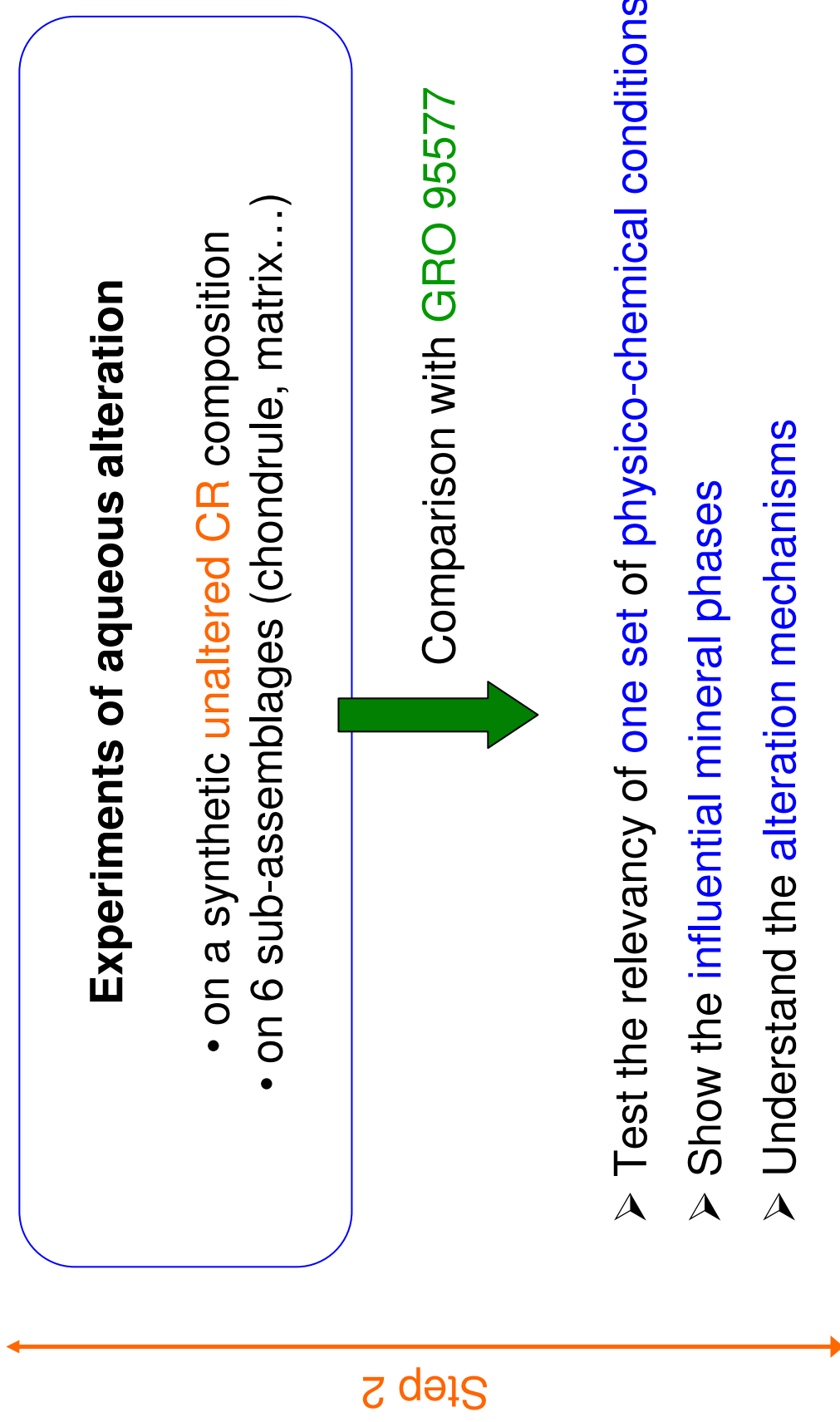
	R	G	CR
Kamacite	0.7	0.2	
Low-Ni kamacite	3.3	2.3	4
Pyrrhotite	0	1.1	
S inter. phases	0.9	5.0	
Magnetite	0	1.1	
Opaque phases	4.9	9.7	



	R	G	CR
Matrix	47.9	45.6	50
Matrix			

- Computation of chemical composition
- **isochemical** alteration
 - composition of the **unaltered CR**

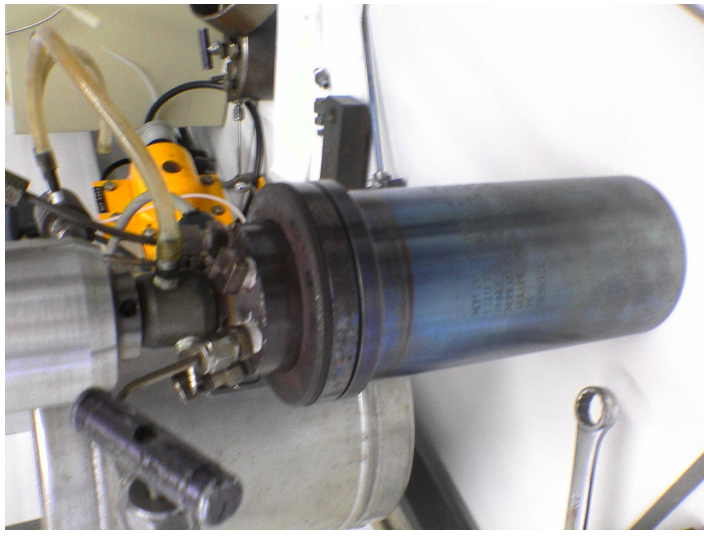
2. Experimental study



2. Experimental study

Experimental conditions

- **Temperature** : 250 °C (see Clayton et al. 1977, Weisberg et al. 1993)
- **Duration** : 1 month
- **Solution** : pure distilled water (fusion of accreted ices)
- **Gaz fugacity** : the mineralogical assemblages set the physico-chemical conditions
= CLOSED SYSTEM
- **R/solution** : 1 or 1/40
- **System** : - preparation in an anoxic glove box
 - hydrothermal Parr bomb
 - initial injection of N₂ → anoxic



2. Experimental study

Experimental conditions

- Different systems

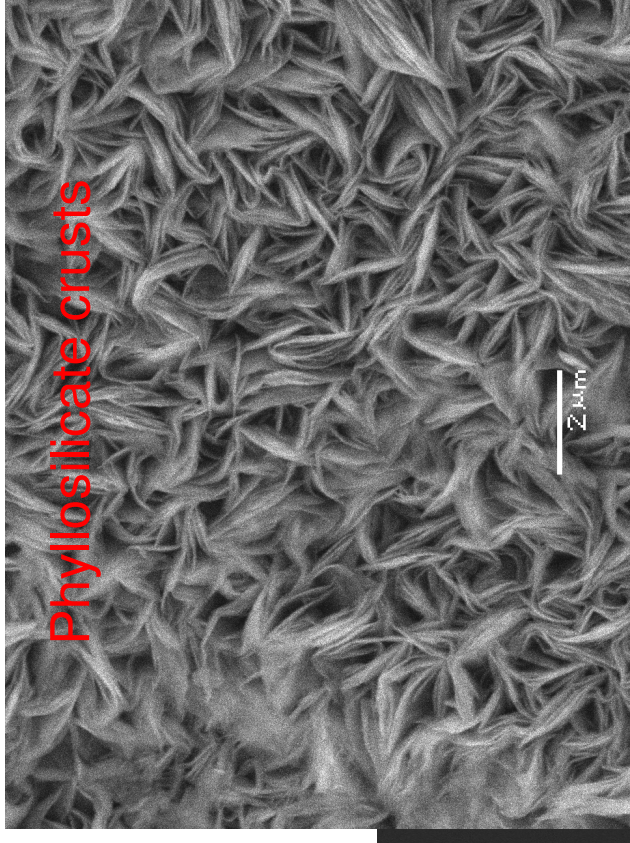
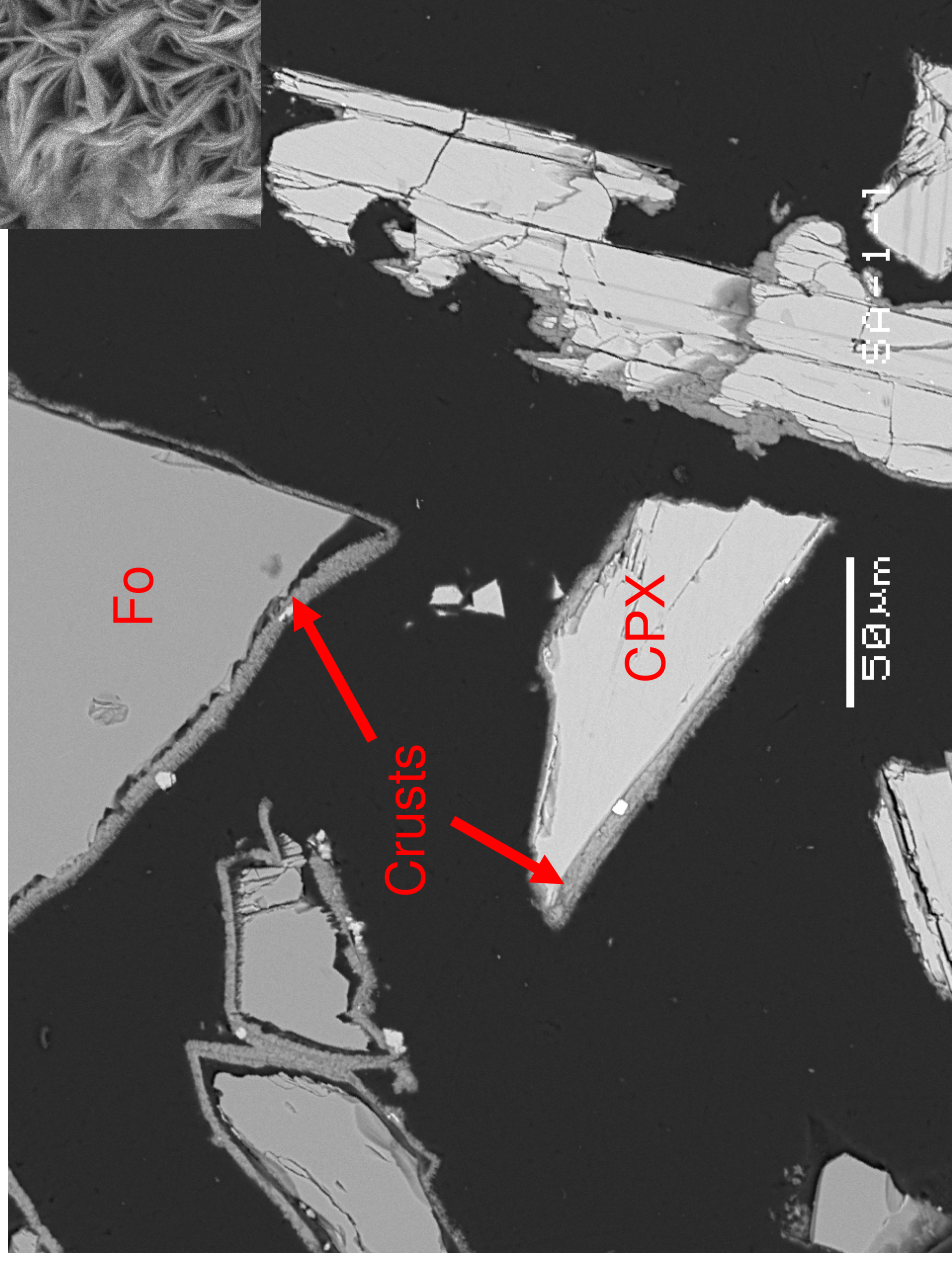


	System	Reagents
SA-1	Silicates chondrule	Fo + CPX + An
SA-2	Silicates chondrule + FeNi	Fo + CPX + An + FeNi
SA-3	Silicates chondrule + sulfides	Fo + CPX + An + Po
SA-4	Silicates chondrule + FeNi + sulfides	Fo + CPX + An + FeNi + Po
SA-5	Matrix	Fo + Fa + FeNi + Po
SA-6	Matrix with organic matter	Fo + Fa + FeNi + Po + O.M.
= Maillard product, Kolb et al. 2005		
A7-3	« Unaltered CR », R/sol°=1	Fo + CPX + An + FeNi + Po
A7-4	« Unaltered CR », R/sol°=1/40	+ Fa + O.M.

2. Experimental study

(1) Alteration within chondrule

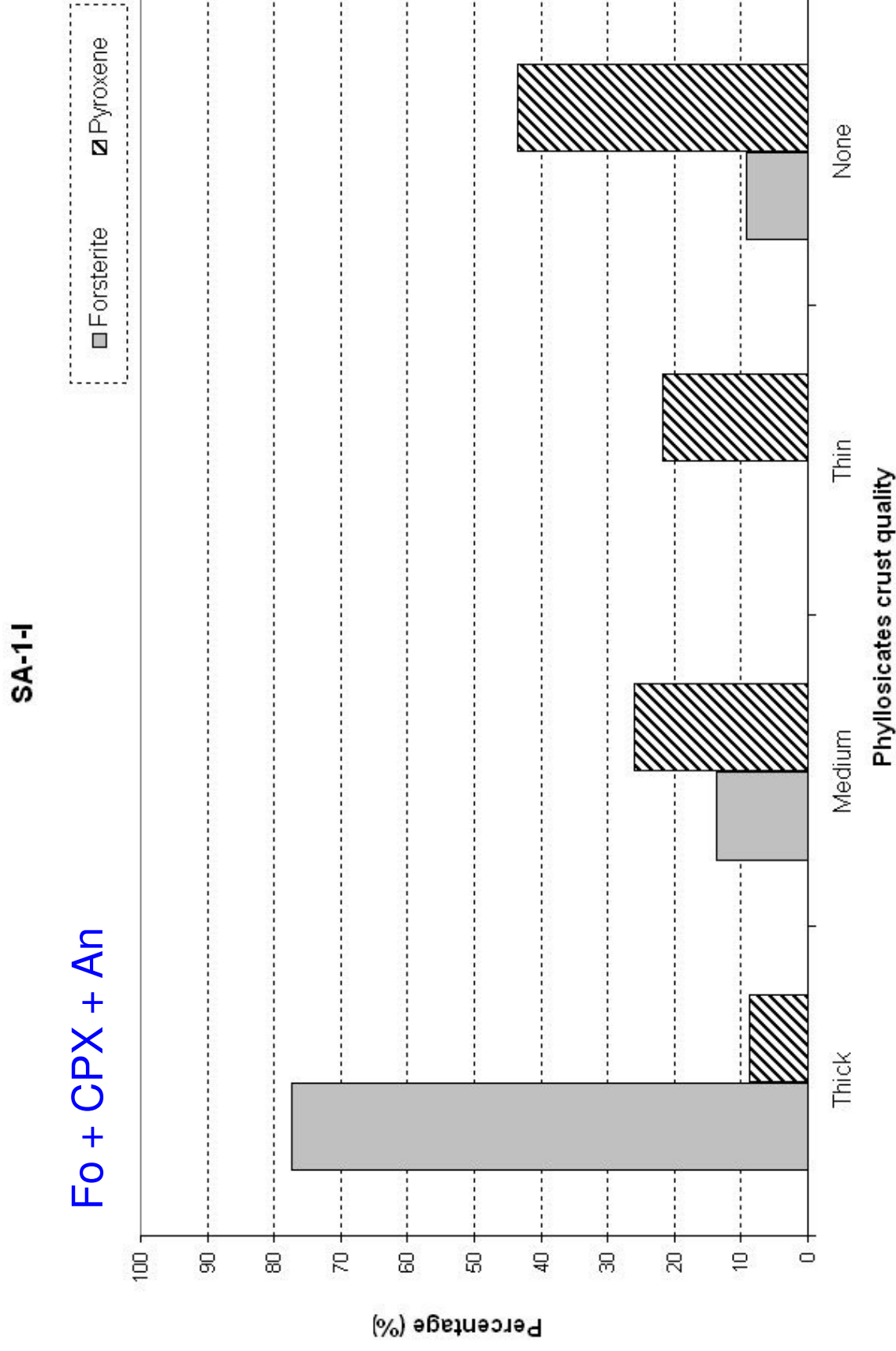
- SA1 : Fo + CPX + An



2. Experimental study

(1) Alteration within chondrule

- Formation of a crust of phyllosilicates

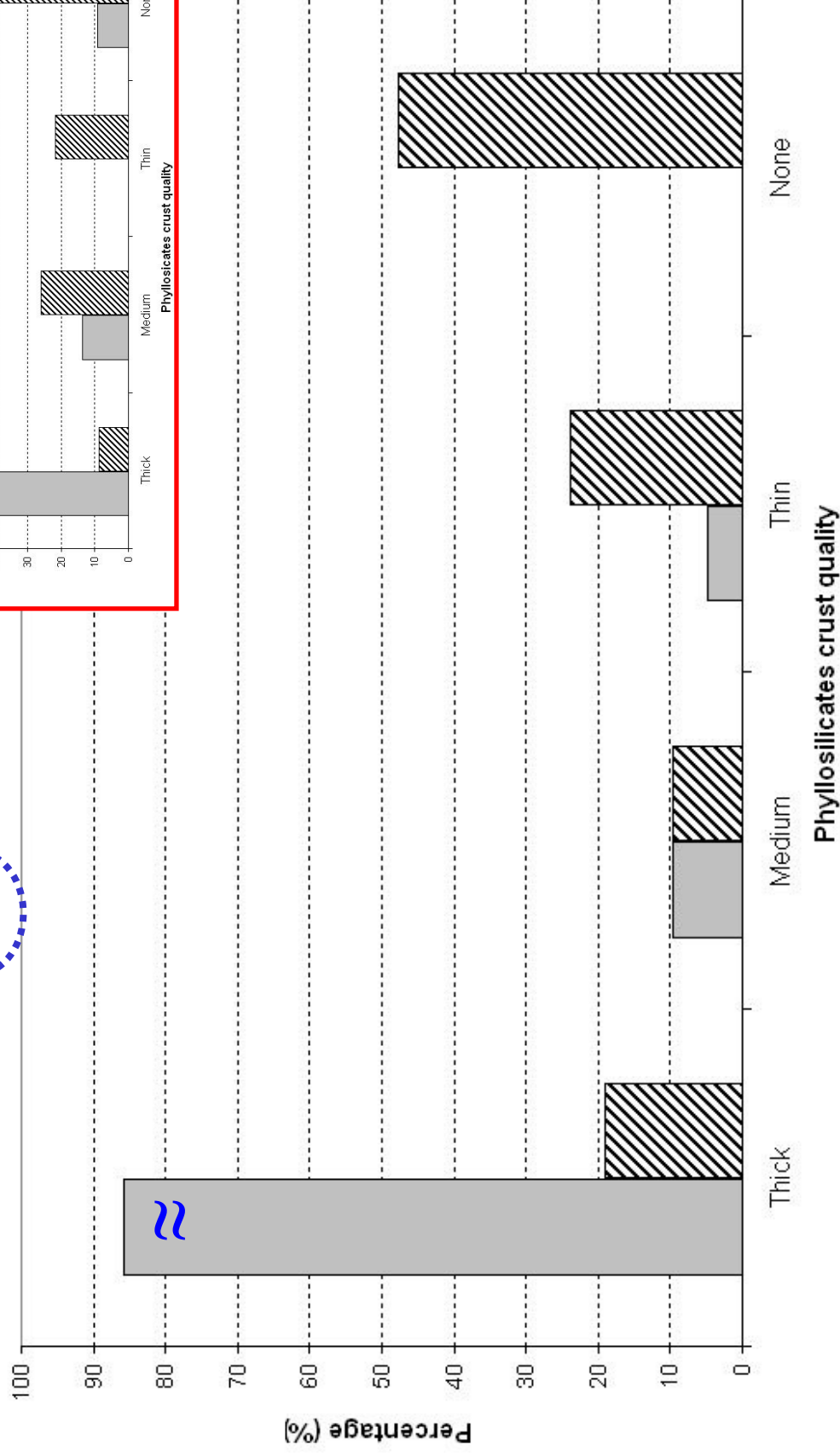


2. Experimental study

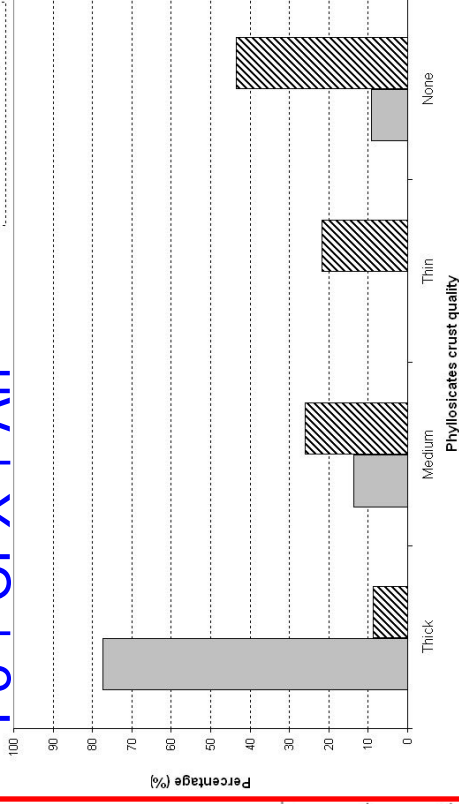
(1) Alteration within chondrule

- Formation of a crust of phyllosilicates

SA-2-I



SA-1-I



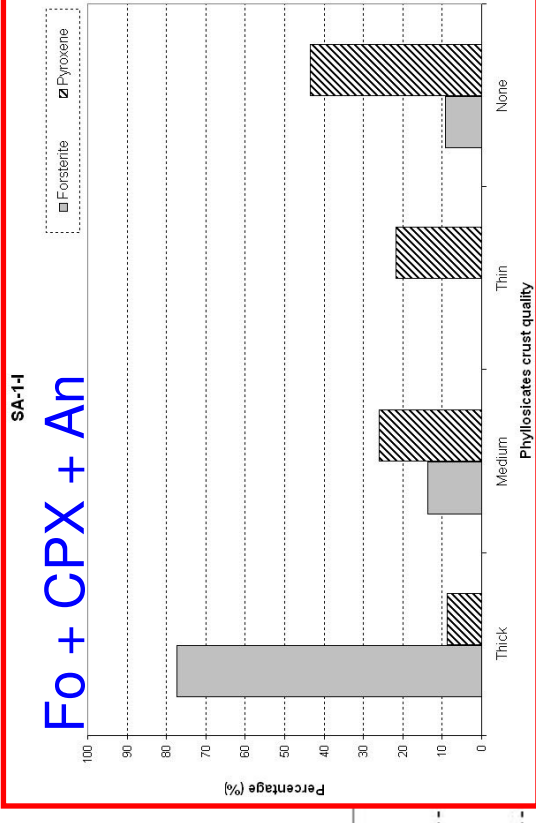
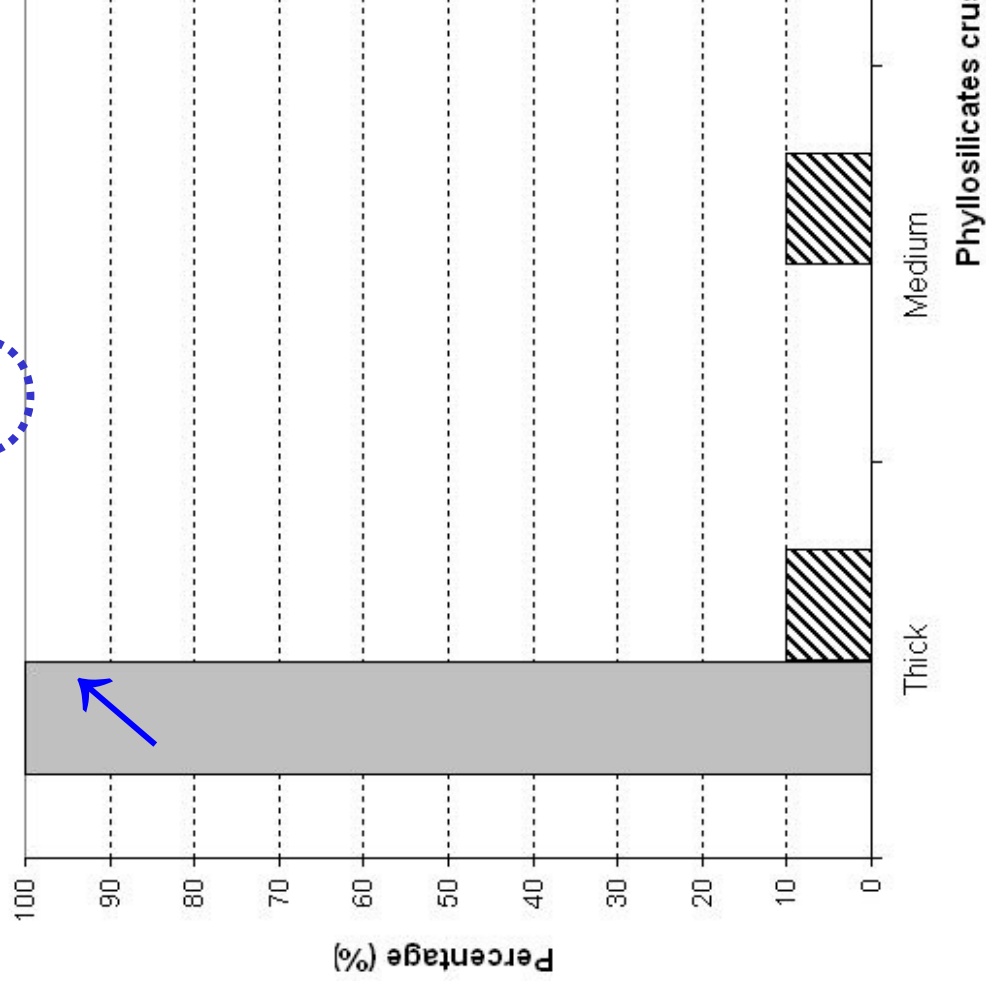
2. Experimental study

(1) Alteration within chondrule

- Formation of a crust of phyllosilicates

SA-3-I

Fo + CPX + An + Po

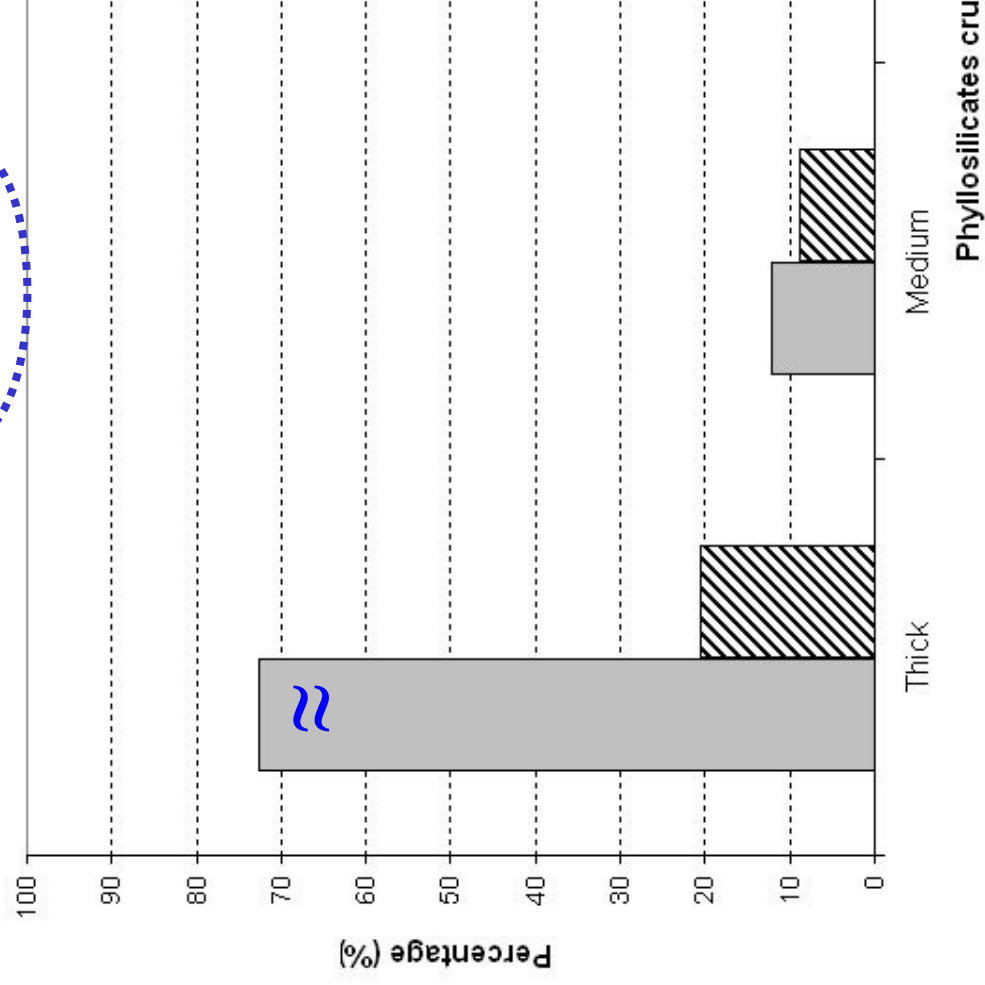


2. Experimental study

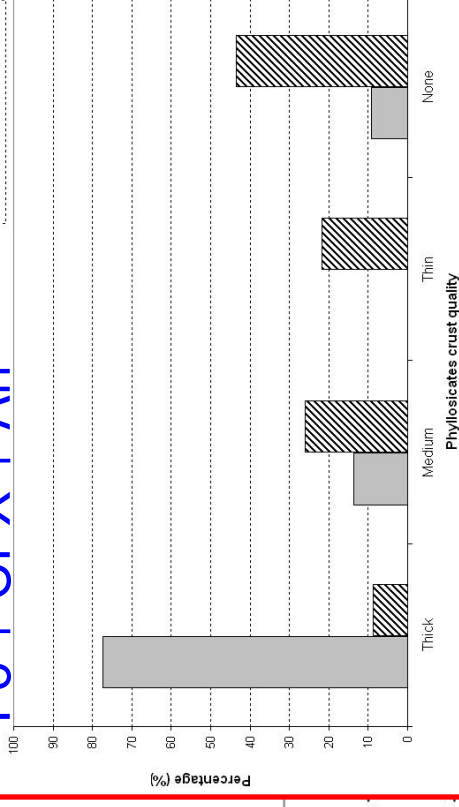
(1) Alteration within chondrule

- Formation of a crust of phyllosilicates

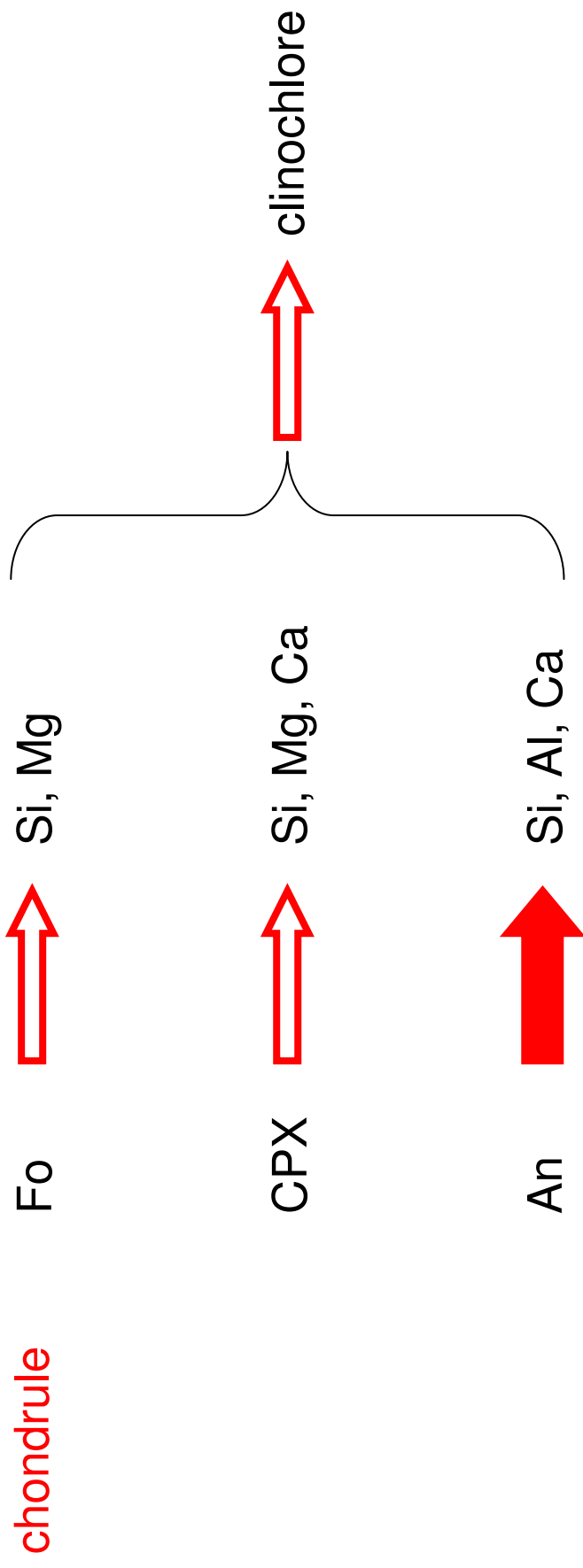
SA-4-I



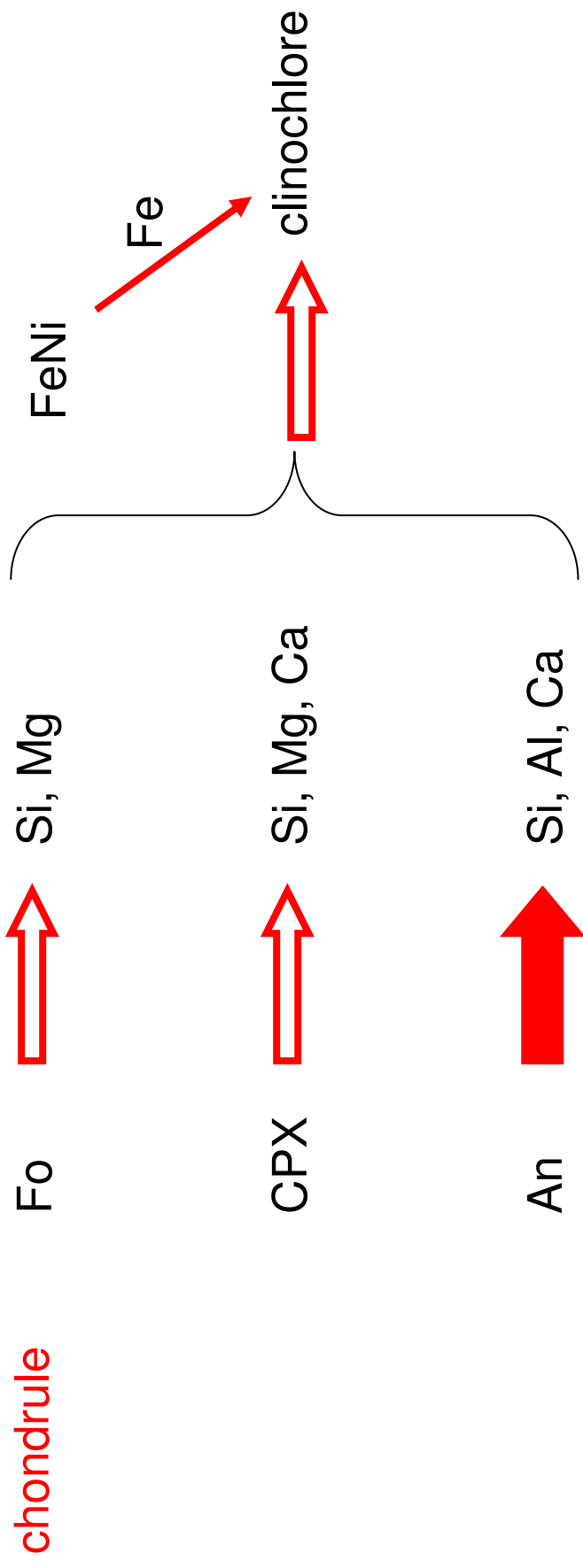
SA-1-I



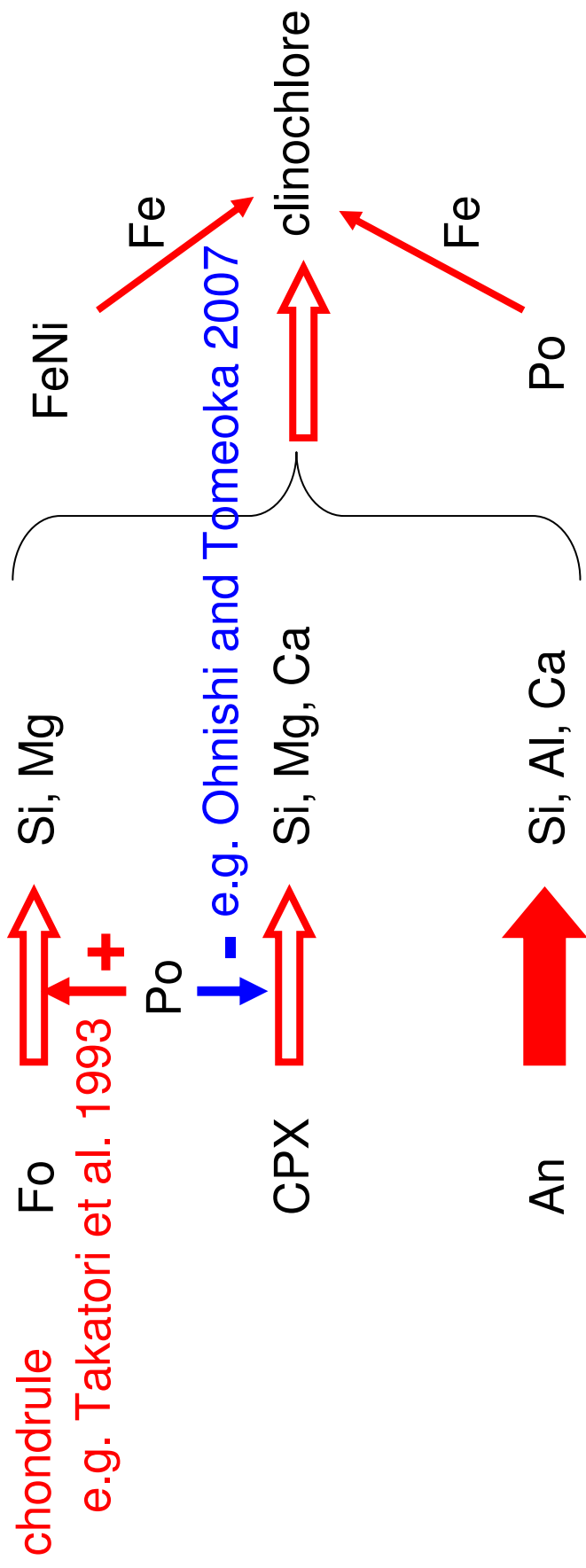
2. Experimental study



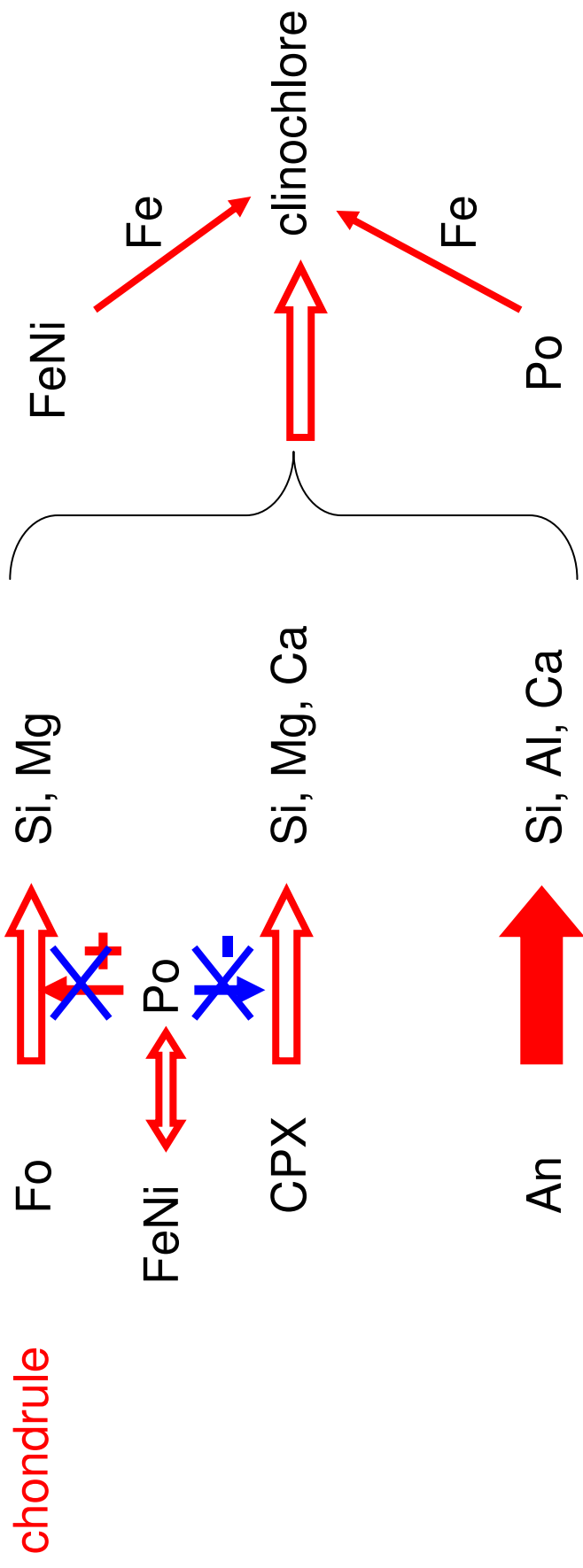
2. Experimental study



2. Experimental study



2. Experimental study

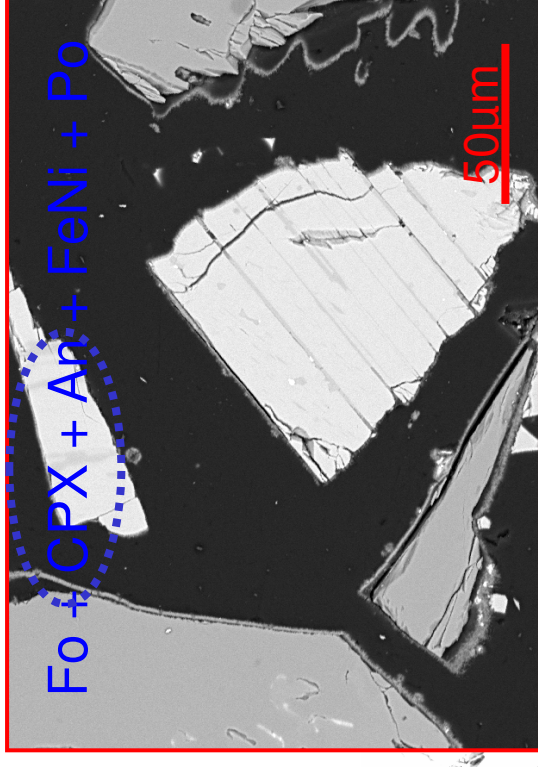
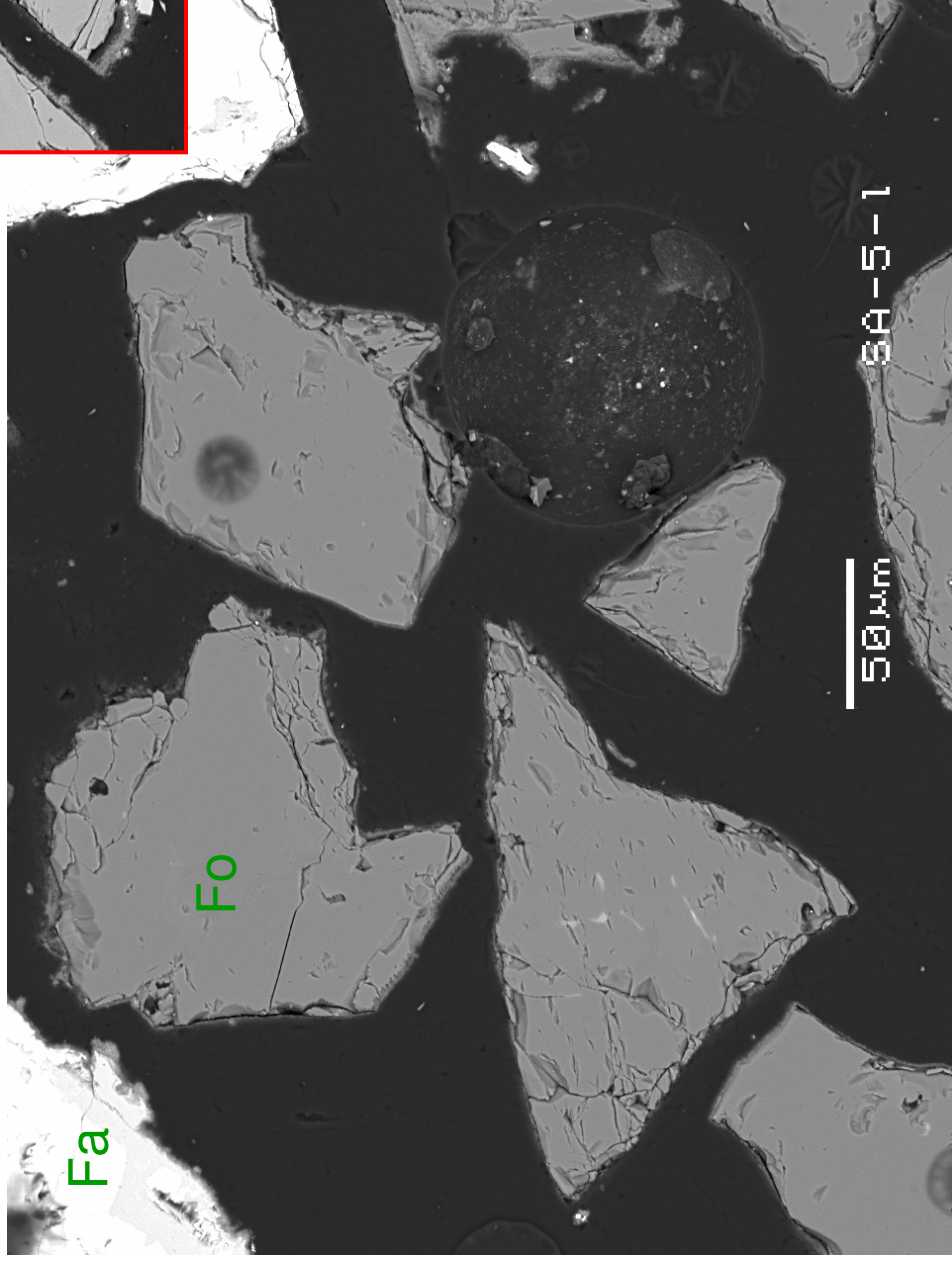


2. Experimental study

(2) Alteration within matrix

- SA-5 : Fo + Fa + FeNi + Po

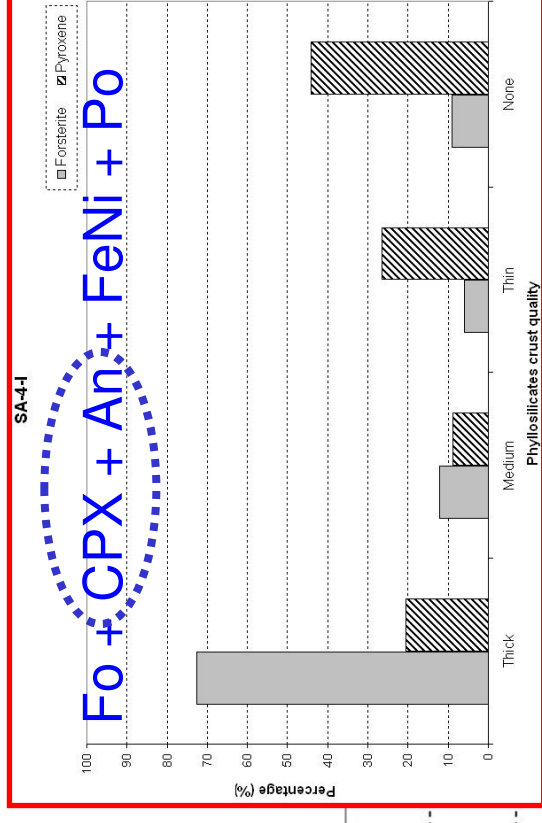
Few crusts !



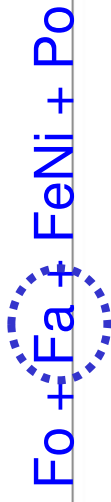
2. Experimental study

(2) Alteration within matrix

- Formation of a crust of phyllosilicates



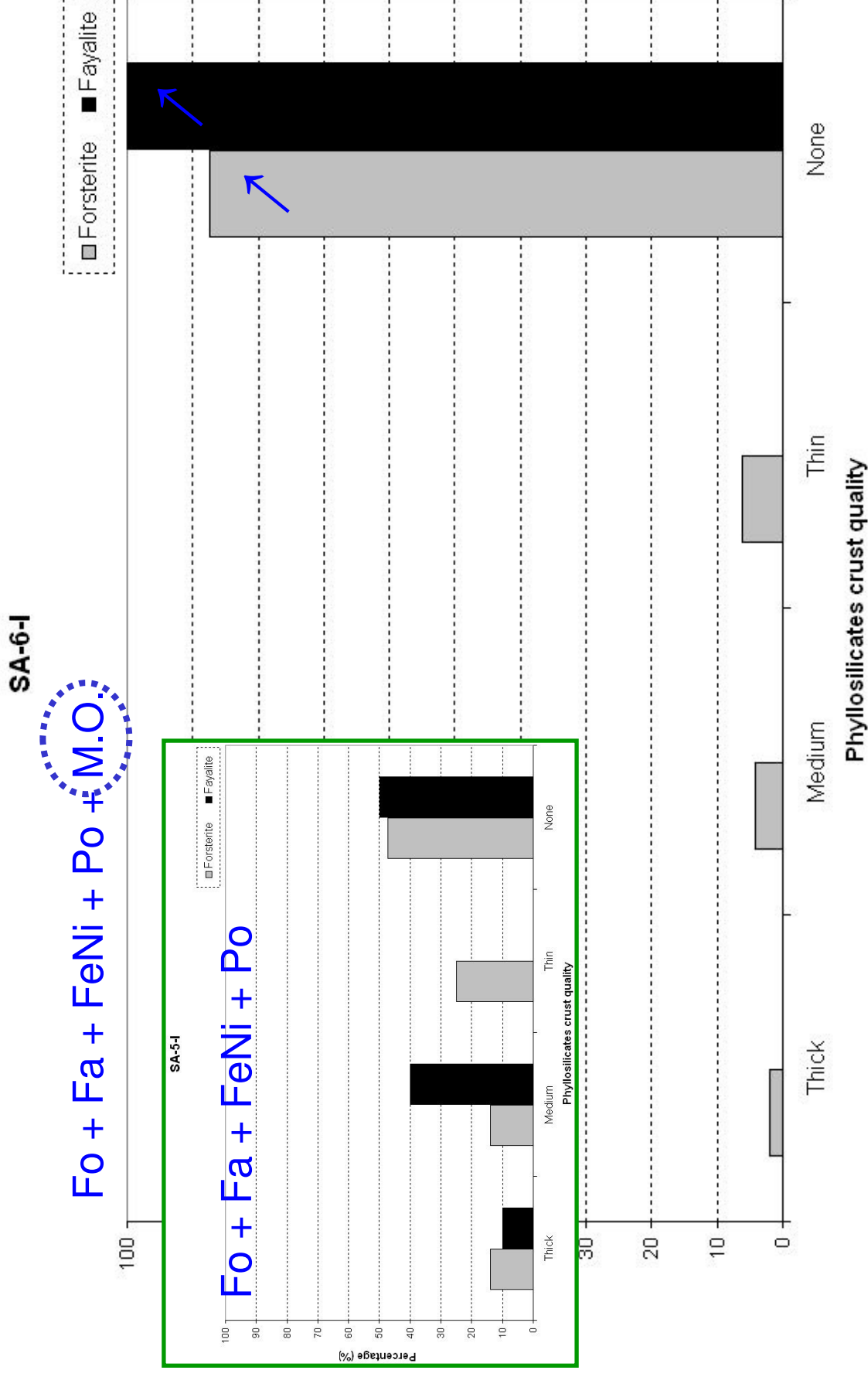
SA-5-I



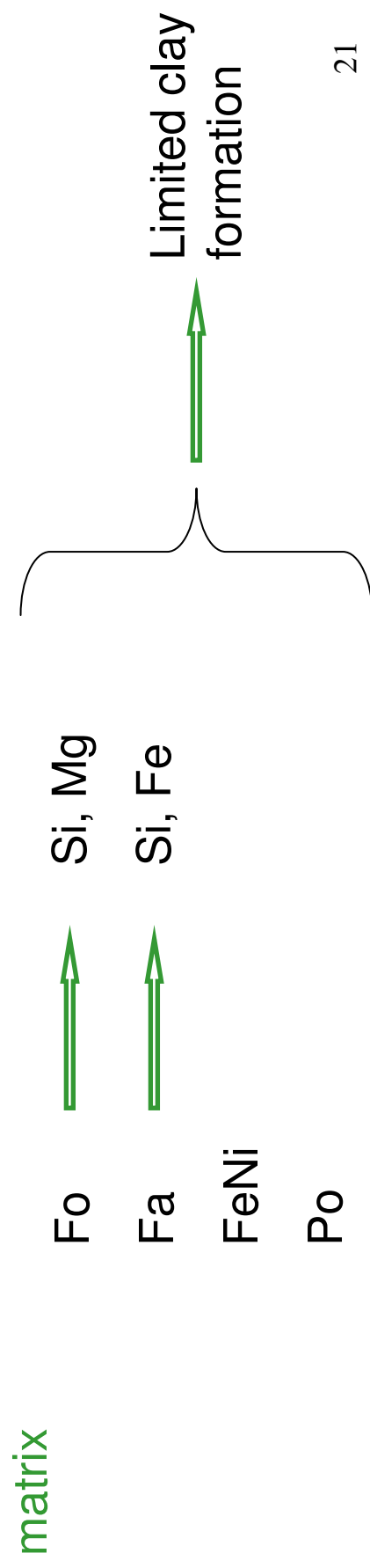
2. Experimental study

(2) Alteration within matrix

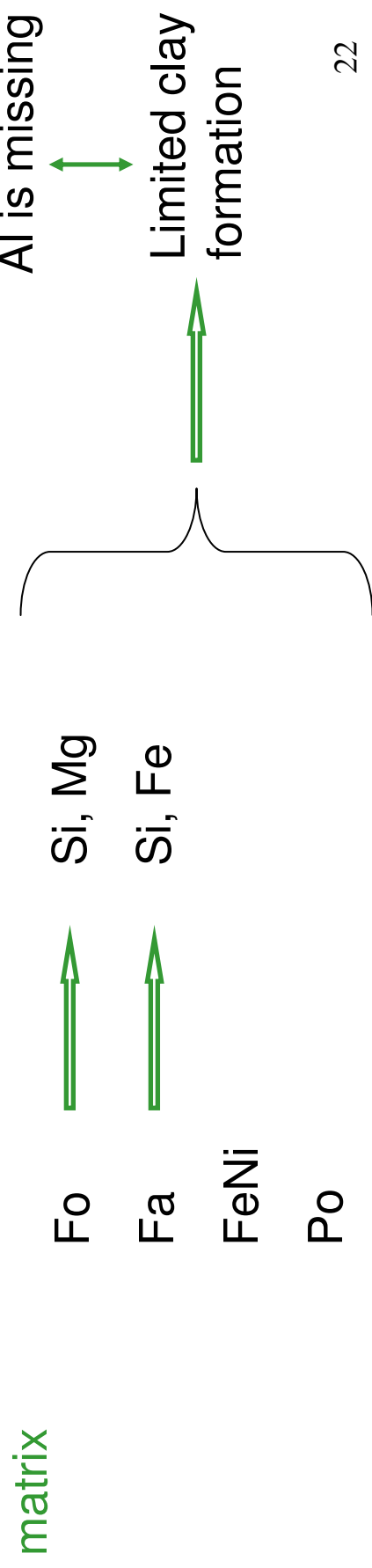
- Formation of a crust of phyllosilicates



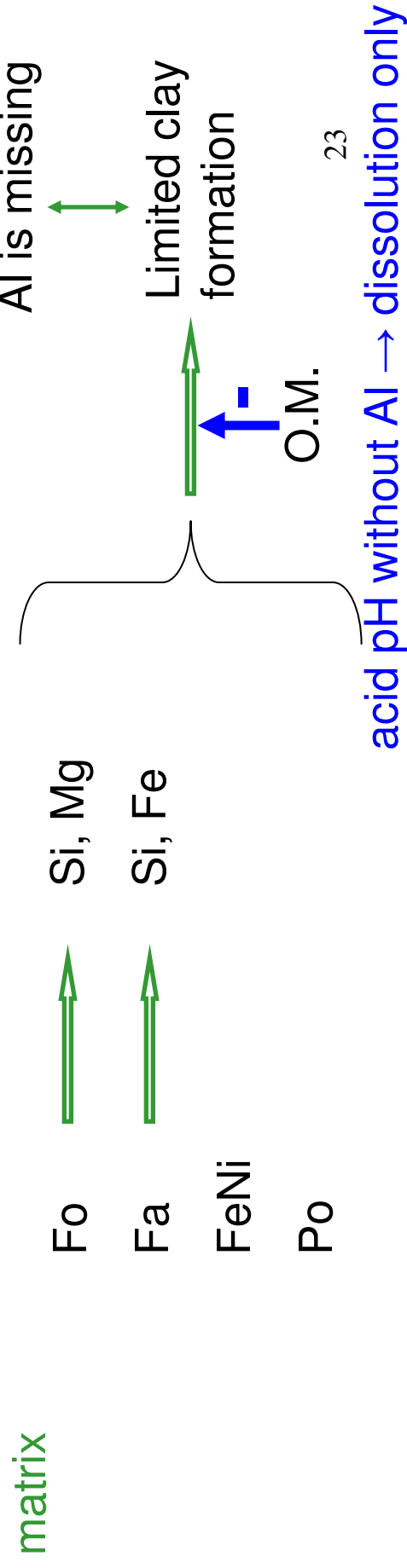
2. Experimental study



2. Experimental study



2. Experimental study

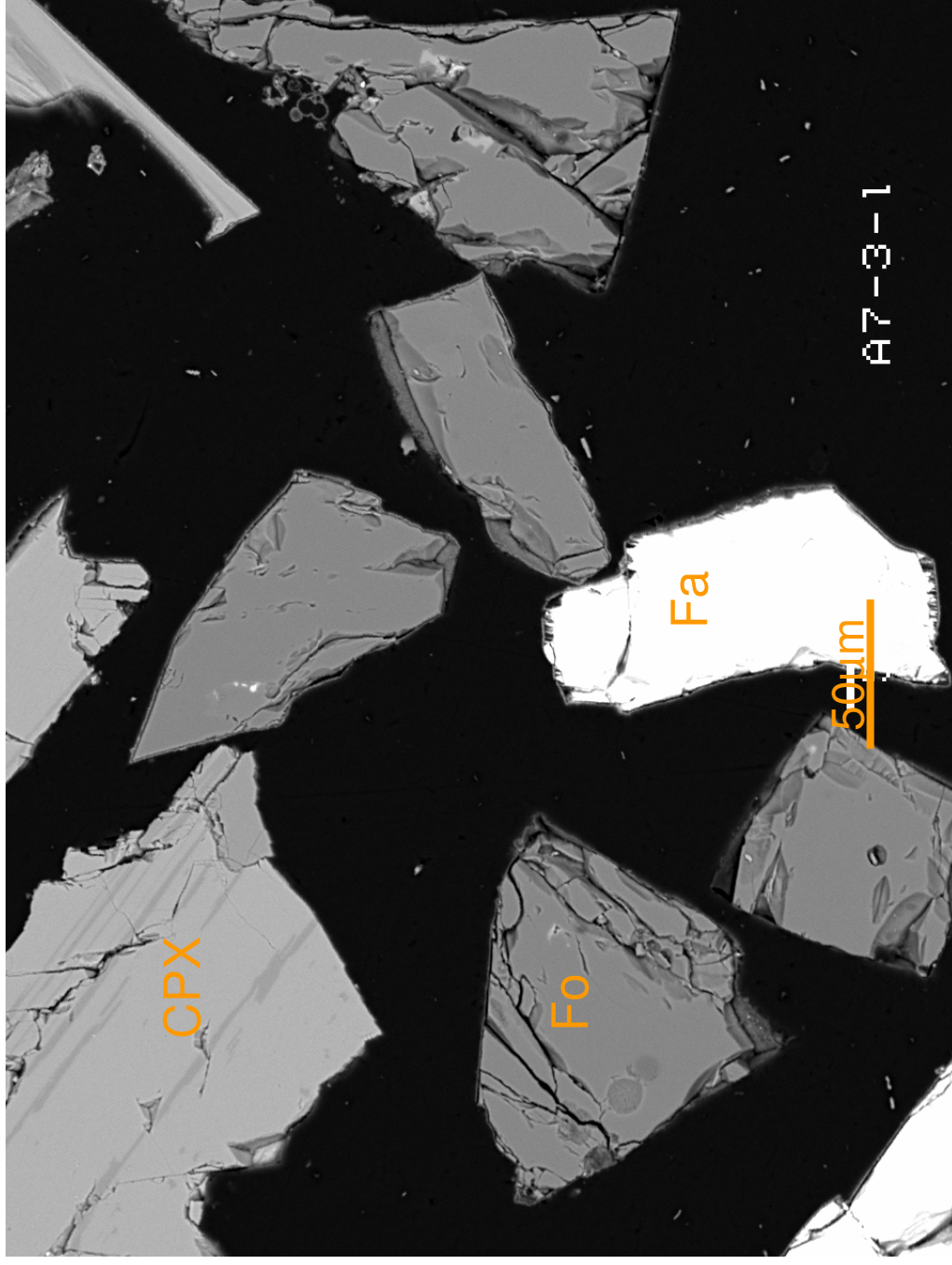


2. Experimental study

(3) Alteration within the *synthetic chondrite*

- A7-3: Fo + CPX + An + Fa + FeNi + Po + O.M., $R/\text{sol}^{\circ}=1$

Few crusts !



2. Experimental study

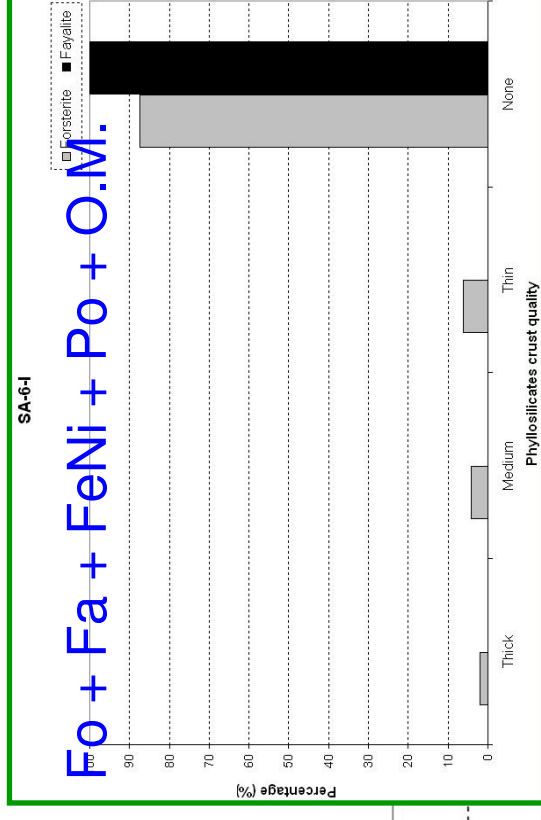
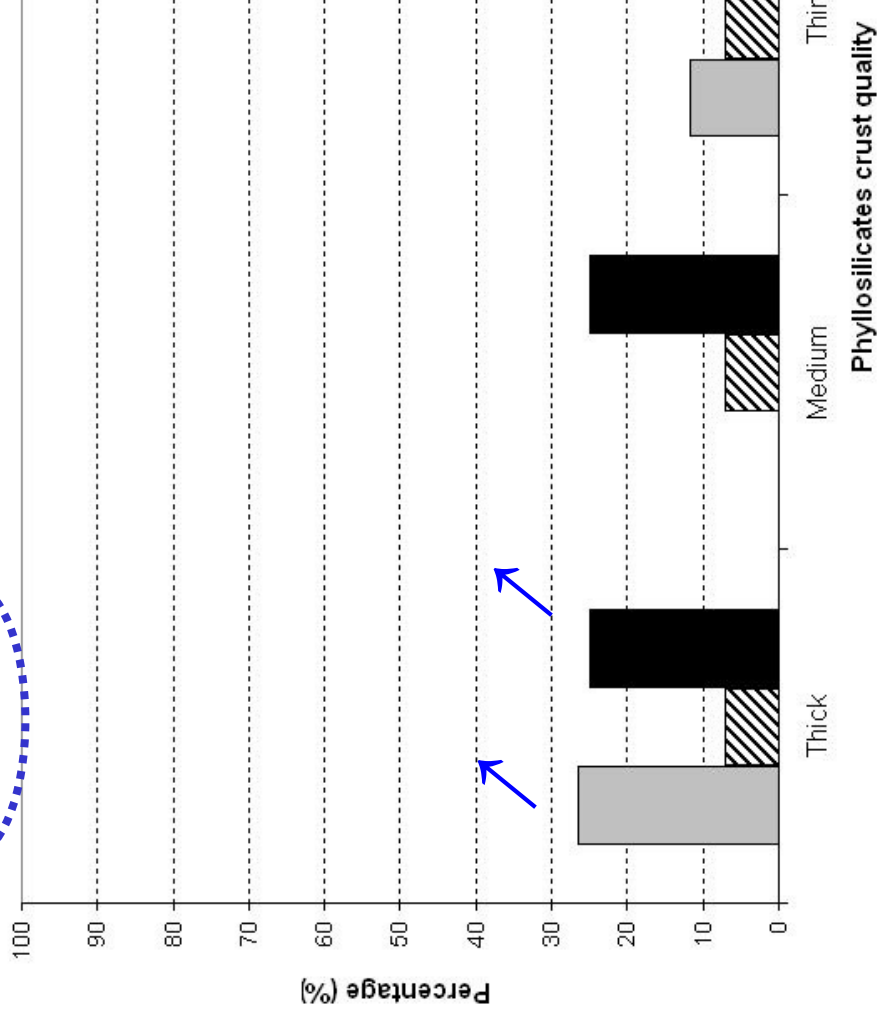
(3) Alteration within the synthetic chondrite

- Few crusts

$R/sol \approx 1$

A7-3-I

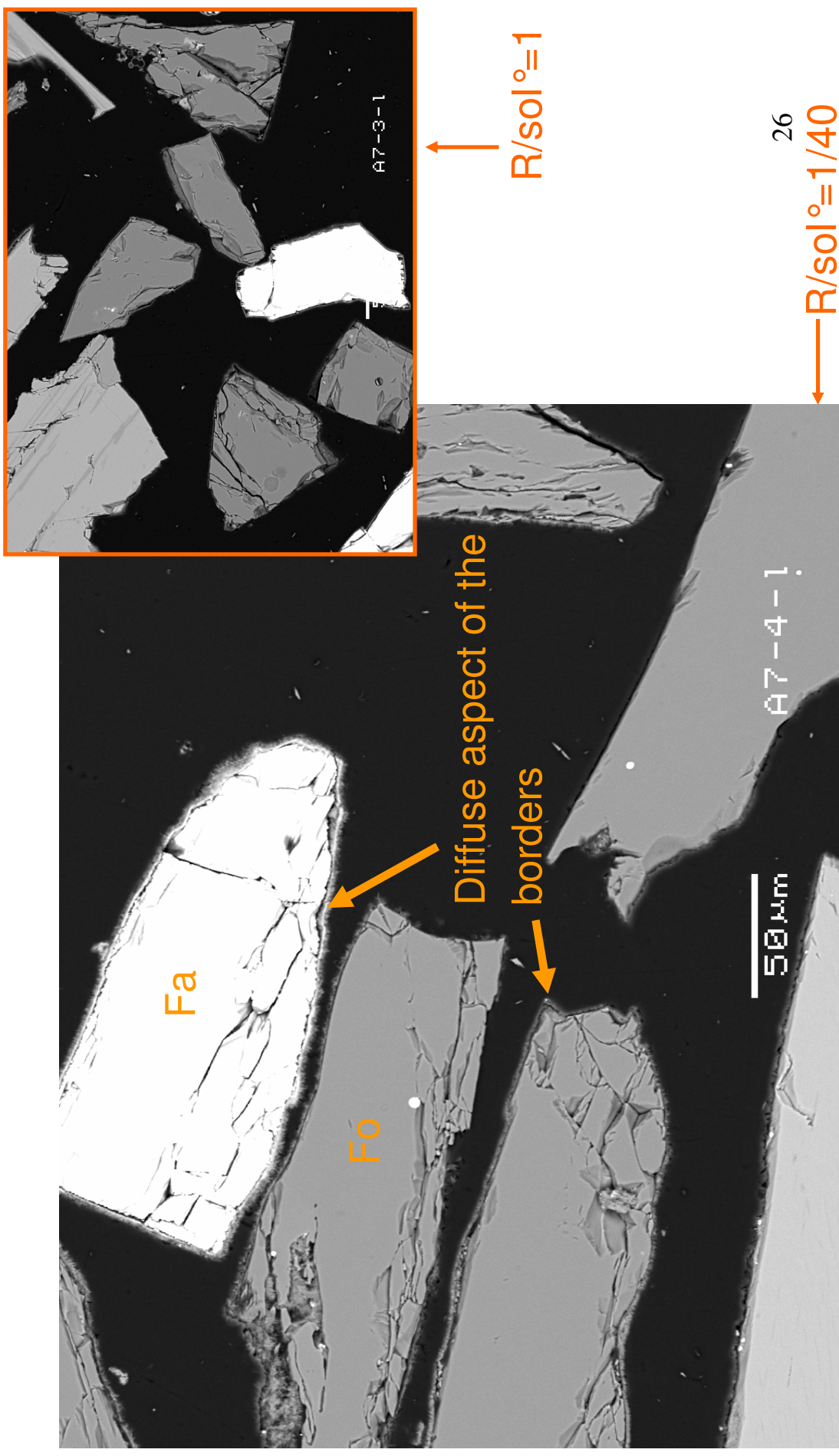
$Fo + CPX + An + Fa + FeNi + Po + O.M.$



2. Experimental study

(3) Alteration within the *synthetic chondrite*

- A7-4 : Fo + CPX + An + Fa + FeNi + Po + O.M., $R/\text{sol}^\circ \approx 1/40$

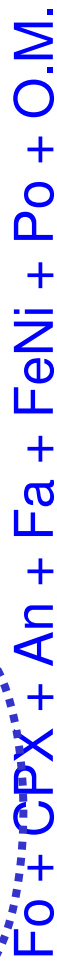


2. Experimental study

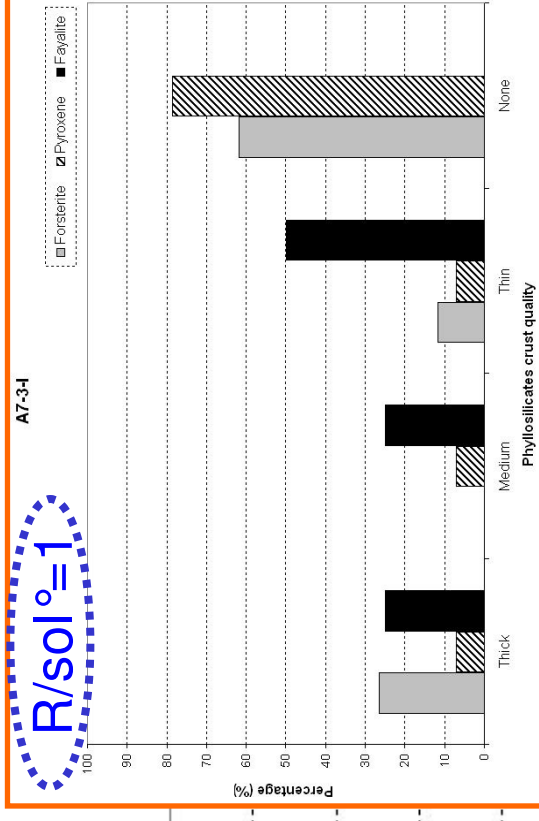
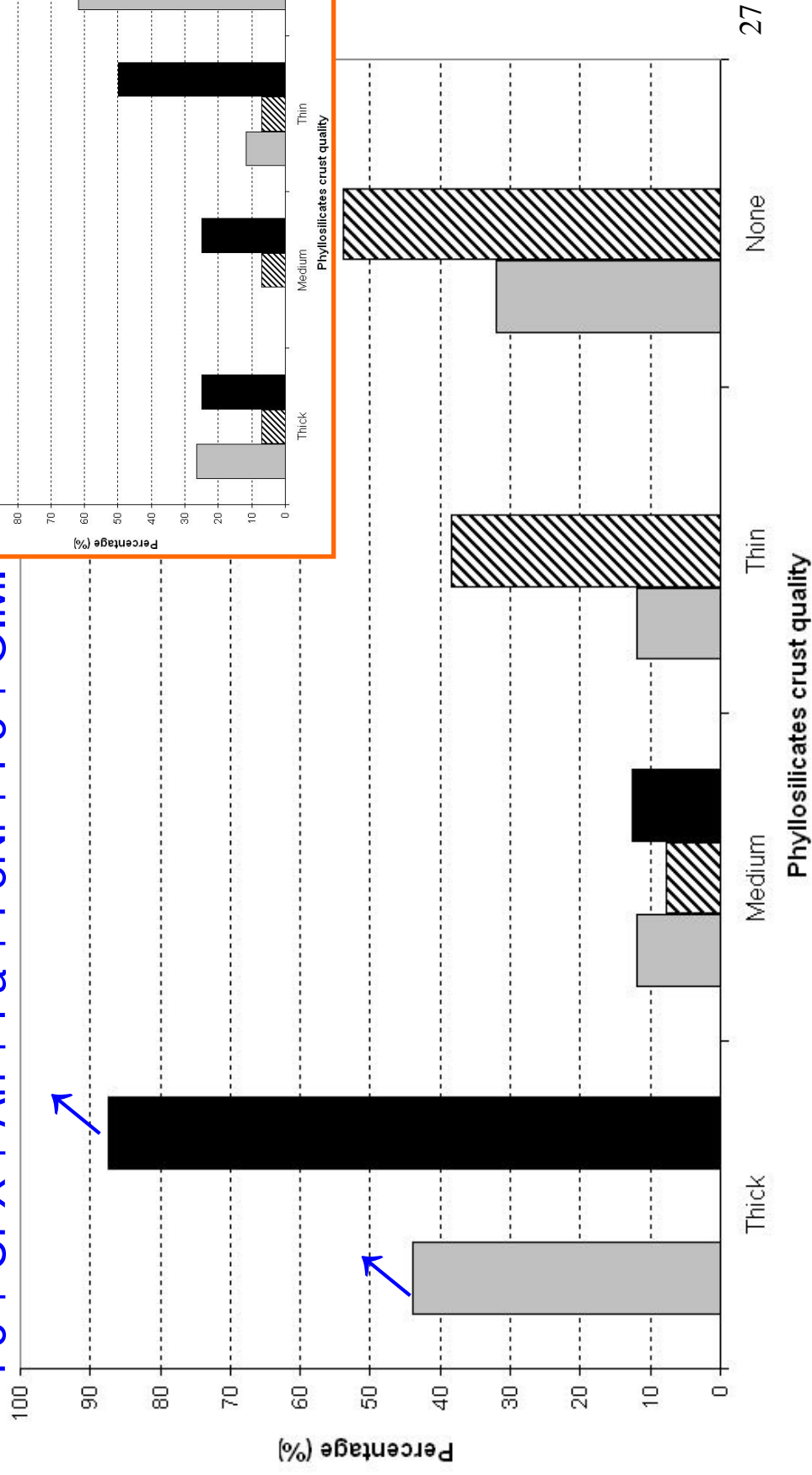
(3) Alteration within the synthetic chondrite

Formation of a crust of pseudo phyllosilicates

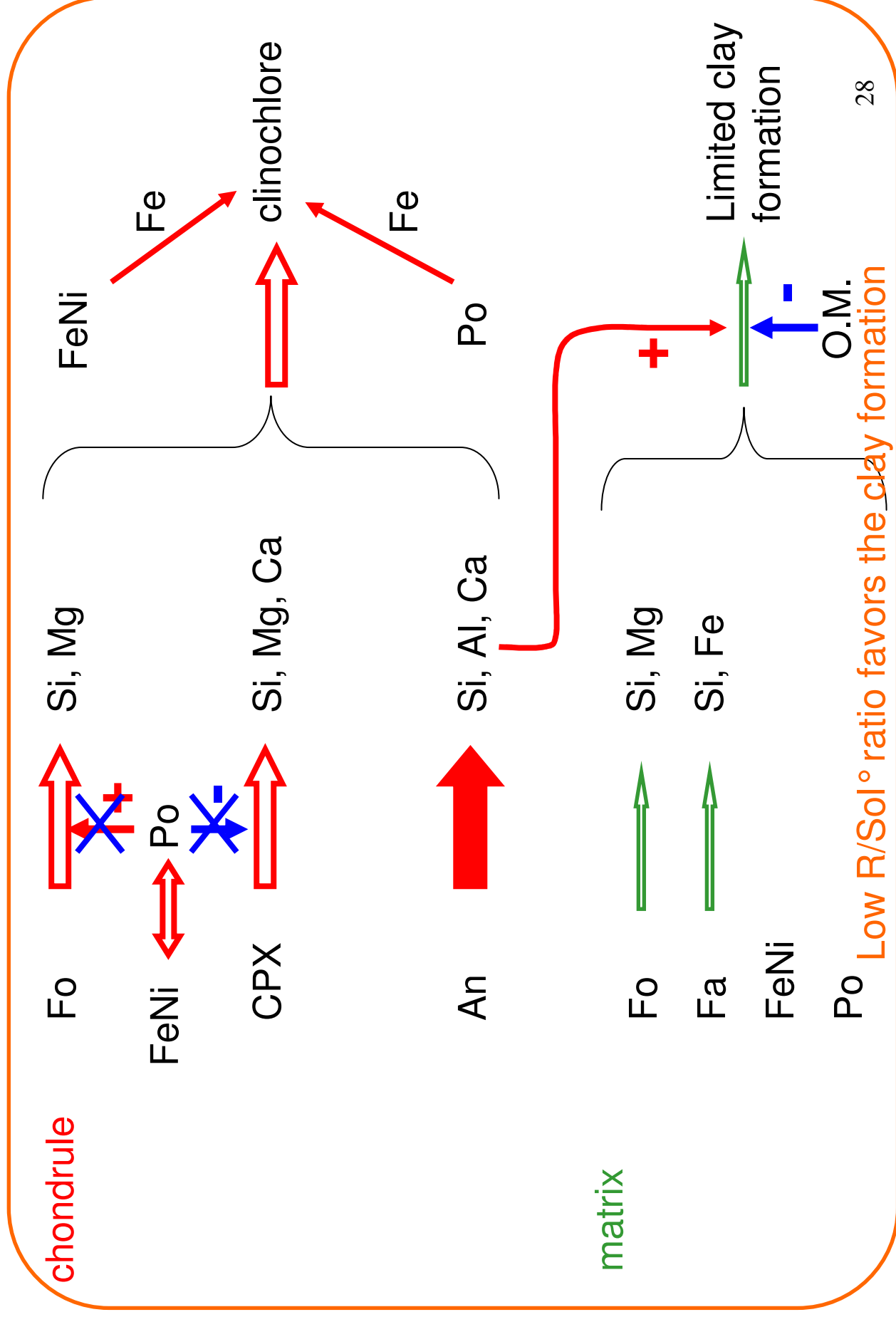
$$R/sol \approx 1/40$$



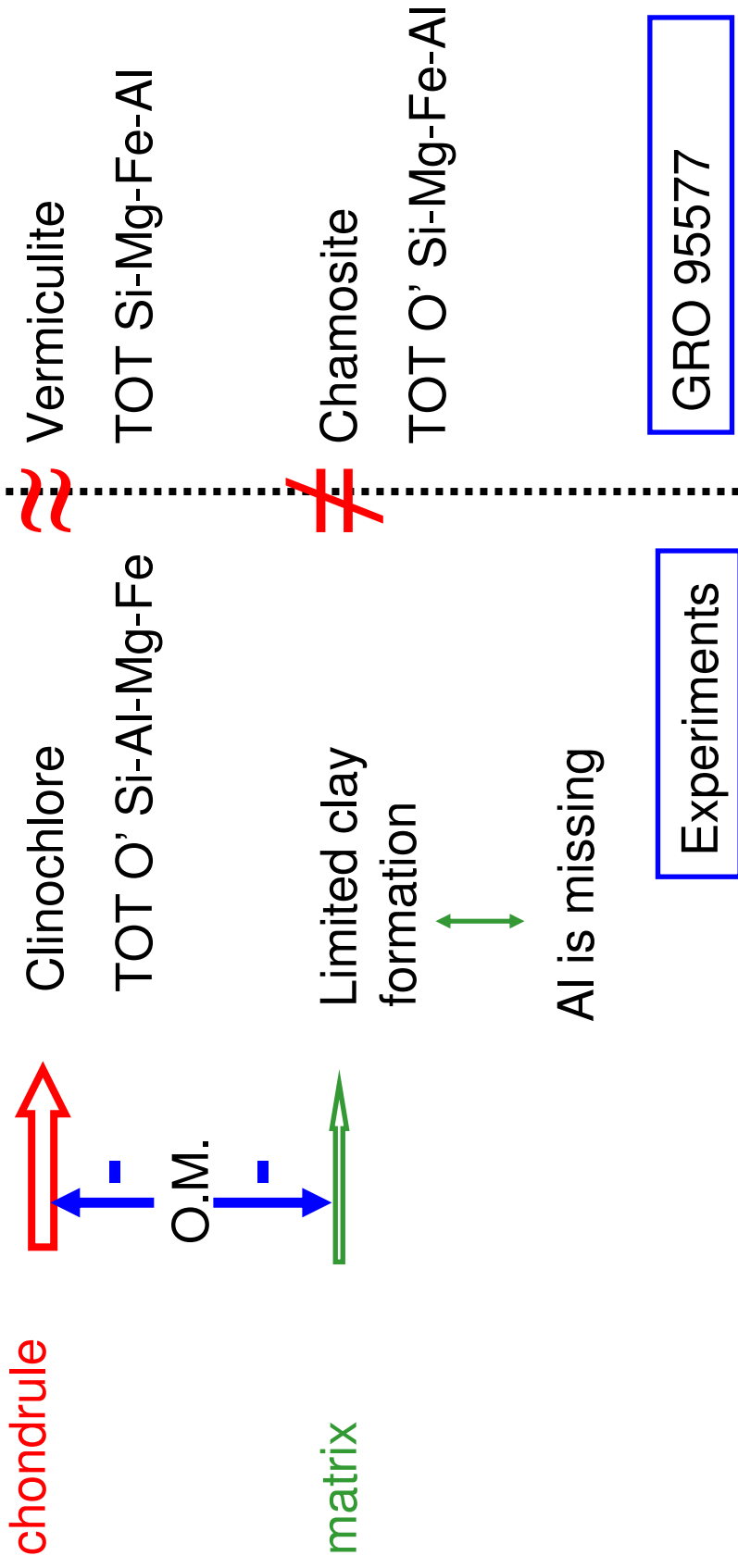
A7-4-I



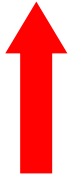
2. Experimental study



2. Experimental study

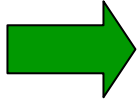


2. Experimental study



Why is there any differences between experiments and GRO 95577 ?

- Limited duration of tests → limited alteration of Mg-bearing minerals (Fo, CPX) et Fe-bearing ones (Fa) compared to Al-bearing ones (An)
- O.M.
- Porosity of the matrix not well reproduced



How to deal with this ...

- Long-duration tests on synthetic chondrites
- Analysis of the O.M. - before and after experiments
 - vs. O.M. in Renazzo and GRO 95577
- Analysis of the matrix of Renazzo and other CRs

3. Geochemical modeling

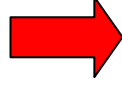
Geochemical modeling using **Geochemist Workbench (GWB)**

- on an **unaltered CR composition**
- on the 6 sub-assemblages (chondrule, matrix...)



Comparison with
reaction products (**Step 2**)

➤ Does the model predict what happened in the experiments ?

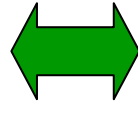


Long-term predictions ?

Application to other carbonaceous chondrite groups ?

3. Geochemical modeling

Systems

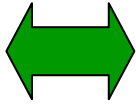


Systems of the experiments (Step 2)

	System	Phases
SA-1	Silicates chondrule	Fo + CPX + An
SA-2	Silicates chondrule + FeNi	Fo + CPX + An + FeNi
SA-3	Silicates chondrule + sulfides	Fo + CPX + An + Po
SA-4	Silicates chondrule + FeNi + sulfides	Fo + CPX + An + FeNi + Po
SA-5	Matrix	Fo + Fa + FeNi + Po
SA-6	Matrix with organic matter	Fo + Fa + FeNi + Po + O.M.
A7-3	« Unaltered CR », S/sol°=1	Fo + CPX + An + FeNi + Po
A7-4	« Unaltered CR », S/sol°=1/40	+ Fa + O.M. ³²

3. Geochemical modeling

Physico-chemical conditions



Conditions of the experiments (Step 2)

- **Temperature** : 250 °C
- **Solution** : pure deionized water
 $1\text{e-}9$ mol Ca^{2+} , Fe^{2+} , Mg^{2+} , SiO_2aq , Al^{3+} , Ni^{2+} , SO_4^{2-}
- **Fugacity in gas** : the mineralogical assemblages set the physico-chemical conditions
= closed system
 $\log f\text{O}_{2\text{g}} = -6$
- **Rock/solution** : 1 or 1/40
- **1 month**

3. Geochemical modeling

Work on thermodynamic data

Use data from thermo.dat = thermodynamic database of **GWB**



Use EQ 3/6 software

Compute **log K** for

- **Kamacite83** : $\text{Fe}_{0.83}\text{Ni}_{0.17}$
considering it as a solid solution between Fe^0 and Ni^0
- **Pentlandite** : $\text{Fe}_{0.5}\text{Ni}_{0.5}\text{S}$
considering it as a solid solution between FeS and NiS
- **Organic matter** : - benzene (aq)
 - phenol (aq)
 - toluene (aq)
 - CH_3COOH (aq) but mostly IOM in chondrites !

3. Geochemical modeling

Non oxidative kinetic laws for dissolution

$$\text{Law} = S * k * (1 - Q/K)$$

	S (cm ² /g)	k (mol/cm ² .s)	Ea (J/mol)
diopside	87	10 ^{-14.15}	62760
forsterite	87	10 ^{-13.5}	62760
fayalite	66	10 ^{-14*}	62760*
anorthite	98	10 ^{-12.55}	62760
pyrrhotite	31	10 ⁻¹⁴	63000
kamacite 83	41	10 ^{-15*}	63000*

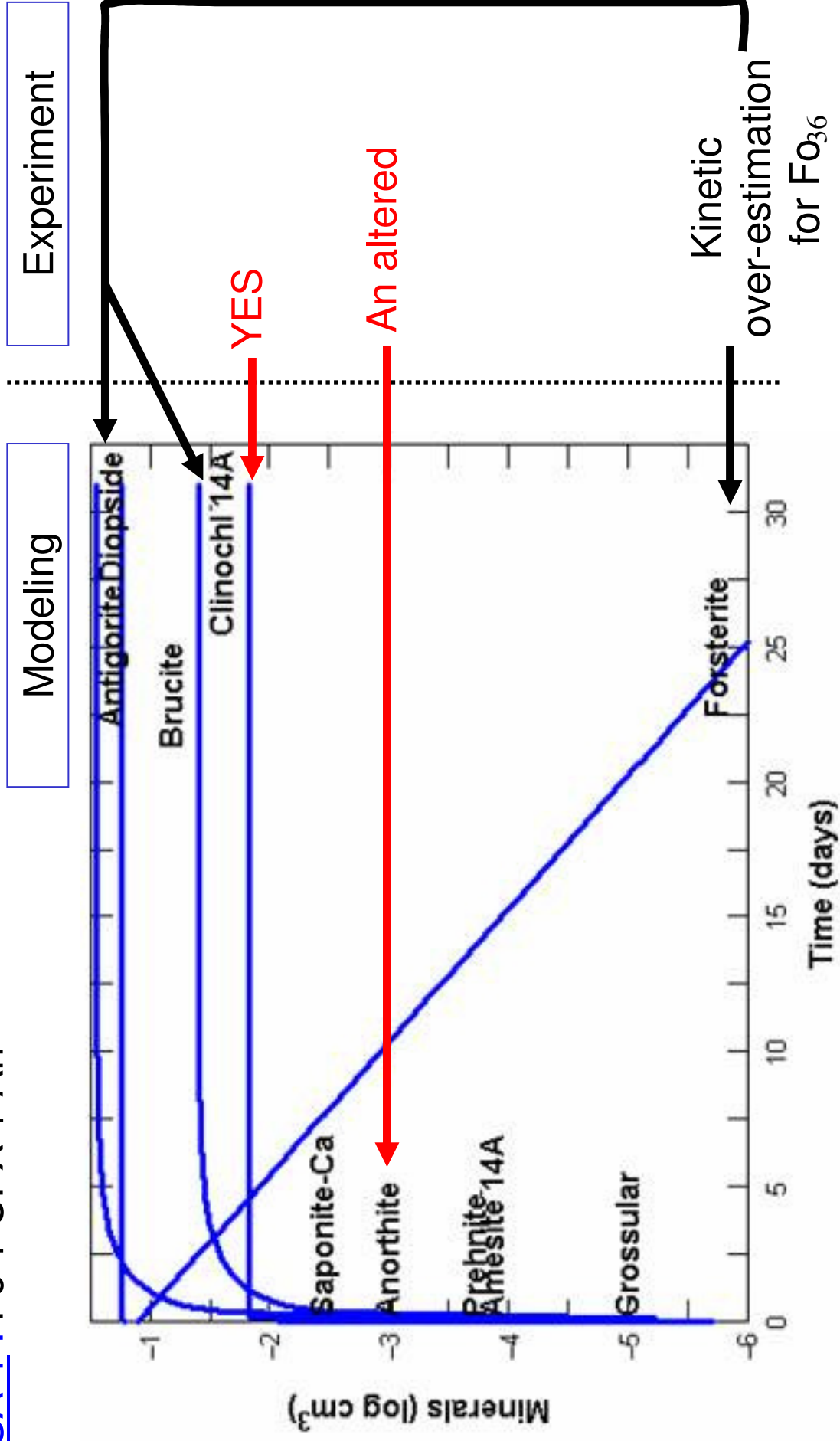
Sources : Lasaga et al. (1994), Janzen et al. (2000)

*Approximated

3. Geochemical modeling

(1) *Alteration within chondrule*

SA-1 : Fo + CPX + An



3. Geochemical modeling

Agreement between modeling and experiments

- crystallization of clinocllore
- alteration of anorthite

•Discrepancy between modeling and experiments

- over-estimation of the kinetic law of dissolution for Fo (nanometric protective layer)
- Transition State Theory used by GWB ► surface properties no taken into account



Work on kinetic laws + add info on surfaces + add info on I.O.M.



Agreement modeling vs. experiments for the other systems



Long-term predictions

Application to other carbonaceous chondrite groups

Conclusions and perspective studies

- Mostly isochemical process during alteration from Renazzo → GRO 95577
 - ➡ heat given by radiogenic decay of ^{26}Al (not accretion)
- Composition of the unaltered CR body estimated
- T=250°C and anoxic conditions are likely
- Importance of the feldspathic mesostasis (Al)
- Importance of the O.M. (wet silicate surfaces)
- Importance of sulfides (acid medium which favors Fe dissolution)
- Importance of the interaction between kamacite-sulfides (high affinity)
 - ➡ SOON, tests at 100°C and at various I.O.M.
- GWB modeling is nearly consistent with natural alteration
 - ➡ SOON, long-term modeling and application to other CCs

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